PATENT ABSTRACTS OF JAPAN

(11)Publication number : 05-117334

(43)Date of publication of application : 14.05.1993

(51)Int.Cl. C08F222/40
C08F210/00

(21)Application number : 03-303911

(22)Date of filing : 24.10.1991

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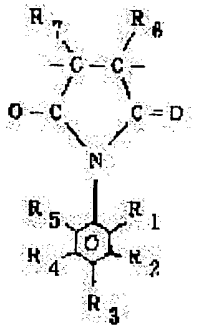
(54) MALEIMIDE-BASED COPOLYMER AND OPTICAL MATERIAL COMPOSED OF THE SAME

(57)Abstract:

PURPOSE: To obtain the subject transparent copolymer, having a specific weight- average molecular weight and low birefringence properties, excellent in heat resistance, etc., and useful as optical materials by blending an N-phenyl- substituted maleimide unit with an N-alkylmaleimide unit arid an α-olefin unit in specific amounts.



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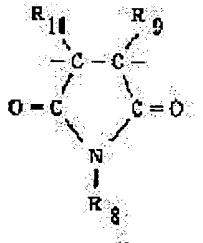

II

III

CONSTITUTION: The objective copolymer is obtained by blending (A) one or more N-phenyl-substituted maleimide units-expressed by formula I (R1 to R7 are H, halogen, carboxylic acid or 1-8C alkyl) with (B) one or more N- alkylmaleimide units expressed by formula II (R8 to R10 are same as R1) and (C) an α-olefin unit expressed by formula III (R11 and R13 are H or 1-6C alkyl). The amounts of the components are 30-98mol% total amount of the components (A) and (B) and 70-2mol% component (C) at (100/0) to (1/99) molar ratio of the components (A/B). The weight-average molecular weight expressed in terms of polystyrene is 1×103 to 5×106.

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LEGAL STATUS

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DETAILED DESCRIPTION

[Detailed Description of the Invention]
[0001]
[Industrial Application] This invention is the transparence and low form birefringence which consist of an N-permutation maleimide-olefin system copolymer and it, and relates to the optical material excellent in thermal resistance, surface hardness, etc.
[0002]
[Description of the Prior Art] Although glass has generally been conventionally used as an optical material, polymeric materials have come to be used from points, such as productivity, lightweight-izing, and cost, in recent years.
[0003] As such an ingredient, the polymethyl methacrylate (it outlines Following PMMA) and the polycarbonate (it outlines Following PC) are used.
[0004] However, although excelled in an optical property, since glass transition temperature (Tg) is near 100 degree C, thermal resistance of PMMA is inadequate and it receives a limit in use.
[0005] On the other hand, PC has troubles, like the moldability with bad weatherability to which an optical property, especially a birefringence are inferior to which in it compared with PMMA greatly although Tg indicates comparatively high thermal resistance to be near 140 degree C, and surface hardness tends to get damaged low is bad.
[0006] Although Tg is high, or the polymerization object obtained by homopolymerization of a maleimide system monomer until now has a weakly weak mechanical strength, there are coloring, then a said fault and only the object inadequate as polymeric materials is obtained. Then, although copolymerization with a methyl methacrylate or styrene has been considered from a viewpoint of the thermal stabilization of acrylic resin or styrene resin in a maleimide system monomer, the present condition is that the satisfying thing is not necessarily obtained from the problem of transparency, i.e., light transmission, coloring, and a birefringence as an optical material application.
[0007]
[Problem(s) to be Solved by the Invention] The purposes of this invention are transparence and low form birefringence, and offer the optical material excellent in thermal resistance, surface hardness, and a mechanical strength.
[0008]
[Means for Solving the Problem] As a result of inquiring wholeheartedly in view of this problem, this invention persons look at that the copolymer obtained by copolymerization of at least one or more kinds of N-permutation maleimide monomers and an olefin system monomer fills the above-mentioned purpose, it is in them, and they came to complete beginning this invention.
[0009] The configuration unit which consists of at least one sort of the compound shown by the general formula (I) or the general formula (II) this invention Namely, 30 - 98-mol% of the whole copolymer The configuration unit which consists of at least one sort of the compound shown by the general formula (III) is 70-2-mol% of the whole copolymer. It is related with the optical material with which the weight average molecular weight of polystyrene conversion consists of the copolymer and it which have the

outstanding transparency characterized by being or more 1x103 the resin which is 5x106 or less, thermal resistance, surface hardness, and mechanical strength.

[0010] As a compound which gives the configuration unit (I) of the copolymer of this invention N-phenyl maleimide, N-(2-methylphenyl) maleimide, N-(2-ethyl) phenyl maleimide, N-(2-isopropyl) phenyl maleimide, N-(3-methylphenyl) maleimide, N-(3-ethyl phenyl) maleimide, N-(4-methylphenyl) maleimide, N-(4-ethyl phenyl) maleimide, N-(2, 6-dimethylphenyl) maleimide, N-(2, 6-diethyl phenyl) maleimide, N-(2, 6-diisopropylphenyl) maleimide, N-(2, 4, 6-trimethyl phenyl) maleimide, N-carboxyphenyl maleimide, N-(2-chlorophenyl) maleimide, N-(2, 6-dichlorophenyl) maleimide, N-(2-BUROMO phenyl) maleimide, N-(par BUROMO phenyl) maleimide, N-(2, 4-dimethylphenyl) maleimide, PARATORIRU maleimide, etc. are mentioned, two or more sorts can be combined, it can use for a polymerization, and these are not one sort or the thing to which those ratios are limited.

[0011] Among these, since the phenyl maleimide of 2-mono-permutation and 2, and 6-JI permutation is especially excellent in respect of viewpoints, such as transparency and coloring nature, and a materials design of low form birefringence which is mentioned later, it is desirable.

[0012] It does not interfere, even if it copolymerizes the unit given to extent which furthermore does not spoil the purpose of this invention from N-alkylation maleimide shown by the general formula (II) other than the above-mentioned phenyl maleimide.

[0013] As a compound which gives this unit, for example N-methyl maleimide, N-ethyl malei mide, N-n-propyl maleimide, N-i-propyl maleimide, N-n-butylmaleimide, N-i-butylmaleimide, N-s-butylmaleimide, N-t-butylmaleimide, N-n-pentylmaleimide, N-n-hexyl maleimide, N-n-heptyl maleimide, N-n-octyl maleimide, N-lauryl maleimide, N-stearyl maleimide, N-cyclo propyl maleimide, N-cyclo butylmaleimide, N-alkylation maleimide, such as N-cyclohexyl maleimide and N-methyl SHITORAKONIMIDO, is mentioned, two or more sorts can be combined, it can use for a polymerization, and these are not one sort or the thing to which those ratios are limited.

[0014] furthermore, as a compound which gives a configuration unit (III) Isobutene, a 2-methyl-1-butene, 2-methyl-1-pentene, A 2-methyl-1-hexene, a 2-methyl-1-heptene, 1-iso octene, 2-methyl-1-octene, 2-ethyl-1-pentene, a 2-methyl-2-butene, Olefins, such as a 2-methyl-2-pentene, a 2-methyl-2-hexene, ethylene, a propylene, 1-butene, 2-butene, and 1-hexene, are mentioned, among these 1, 2-JI permutation olefin, especially isobutene are used preferably. Moreover, two or more sorts can be combined, it can use for a polymerization, and these olefins are not one sort or the thing to which those ratios are limited.

[0015] It is 30 - 98-mol% of the whole copolymer, and 40 - 75-mol% of the content of configuration (unit I) +(II) of this invention is desirable, and is desirable. [especially 50 - 70 mol% of] When configuration (unit I) +(II) exceeds 98-mol %, since it becomes weak and the thermal resistance of resin falls less than [30 mol %], the resin to generate is not desirable.

[0016] Moreover, if required, copolymerization of other vinyl system monomers can be carried out to a copolymer in the range which does not spoil the purpose of this invention.

[0017] As other vinyl system monomers, they are styrene, alpha methyl styrene, and vinyltoluene. One or more sorts of compounds chosen from vinyl ether, such as vinyl ester, such as acrylic ester, such as 1,3-butadiene, isoprenes and these halogenation derivatives, and a methyl methacrylate, vinyl acetate, and benzoic-acid vinyl, and the methyl vinyl ether, a vinyl chloride, a vinylidene chloride, a maleic anhydride, and acrylonitrile are mentioned.

[0018] Although the polymerization of these monomers can adopt emulsion-polymerization a well-known polymerization method, for example, a bulk-polymerization method, a solution polymerization method, a suspension-polymerization method, or a method, especially a solution polymerization method is desirable.

[0019] The maleimide system copolymer by this invention is excellent in transparency, and has a high refractive index, and since (YI) and the birefringence are [whenever / yellow] small, it is preferably used as an optical material.

[0020] By generally introducing a phenyl group like the benzene ring as a substituent, or a halogen system element per configuration, the refractive index according to a demand of various kinds of optical

applications can be embodied, and it is not the exception in the optical material of this invention.
[0021] Therefore, also in this invention, a phenyl group can be introduced into a copolymer, and a refractive index can be changed from 1.49 to 1.63 by controlling the content.
[0022] About the reduction-ized approach of a birefringence, they are former J.Appl.Polym.Sci. (13), 2541 and 1969, and Plaste. und In Kautschuk, (29), 618 and 1982, and JP,61-108617,A, two or more kinds of the polymers or monomers which have a forward and negative birefringence are blended or copolymerized by suitable presentation, and the approach of offsetting a birefringence seemingly is indicated. For example, according to the above-mentioned publication, as non-aromatic series systems, such as a polycarbonate which has an aromatic series ring in a principal chain, polyphenylene oxide, polyester, polysulfone, and polyether imide, Pori N-alkylation maleimide etc. is indicated as a polymer which has a forward birefringence.
[0023] On the other hand, about the polymer which has a negative birefringence, the polystyrene which consists of monomers which contain the benzene ring other than a polymethyl methacrylate, acrylic-acid (meta) high-class alkyl ester polymer -, Pori 4-vinylpyridine, and Pori beta-vinyl naphthalene in a side chain, polyvinyl toluene, Pori N-phenyl permutation maleimide, etc. are indicated as a non-aromatic series system.
[0024] However, polystyrene or polyphenyl maleimide with which the include angle which chain shaft orientation and the benzene ring make about the monomer which contains these benzene rings [like] in a side chain is important, and is not necessarily indicated to be by JP,61-108617,A do not always take the value of a negative birefringence. For example, in the case of polystyrene, when the benzene ring which is a side chain is in a chain shaft and a parallel direction, it is forward, and when it is perpendicularly, having a negative birefringence is shown theoretically and experimentally by the reference of "solid-state physical properties II of macromolecule" KYORITSU SHUPPAN, Polym.Prep.Jpn., (38), 10 and 3539, and 1989 grades.
[0025] Therefore, it can say that the same is said of a phenyl maleimide system polymer, when there is no substituent in the benzene ring and a maleimide ring and the benzene ring are in it almost in parallel, a substituent is introduced into forward and the suitable location of the benzene ring, and according to steric hindrance, if the conformation of a side chain is controlled like, the thing with almost perpendicular for example, maleimide ring and benzene ring for which it has the value of a negative birefringence is expected.
[0026] In fact, Pori N-(2-methylphenyl) maleimide forward in Pori N-phenyl permutation maleimide and Pori N-(2, 6-diethyl phenyl) maleimide became clear by examination of artificers with detailed having the value of a negative birefringence against the publication of JP,61-108617,A. Moreover, when side-chain conformation was determined using the semiempirical molecular orbital method (AM1, J.J.P.Stewart, QCPE #455), by Pori N-phenyl permutation maleimide, it became clear by 30 degrees and Pori (2-methylphenyl) maleimide that the angle which a maleimide ring and the benzene ring make in the maximum stability conformation is 83 degrees in 65 degrees and Pori (2, 6-diethyl phenyl) maleimide. Moreover, when the polarizability anisotropy of a monomeric unit was calculated using the congener method, by Pori N-phenyl permutation maleimide, by a value, forward Pori (2-methylphenyl) maleimide, and forward Pori (2, 6-diethyl phenyl) maleimide, it became clear that a negative value is shown and it resulted in supporting an experiment. Therefore, by copolymerizing the monomer which has these negative birefringences, and the olefin system monomer which has a forward birefringence, the birefringence was reduced seemingly and it found out that the polymeric materials which were moreover excellent in the physical properties of a mechanical strength or others with installation of an olefin chain could be obtained.
[0027] Furthermore, the maleimide system monomer of at least two or more kinds of alkylation and a phenyl permutation is combined more than plurality, and even if it copolymerizes with an olefin system monomer, it does not interfere.
[0028] As those combination, for example, N-methyl maleimide / N-methylphenyl maleimide / isobutene, N-methyl maleimide / N-(2, 6-diethyl phenyl) maleimide / isobutene, N-cyclohexyl maleimide / N-methylphenyl maleimide / isobutene, N-cyclohexyl maleimide / N-(2, 6-diethyl phenyl)

maleimide / isobutene, Combination, such as N-ethyl malei mide / N-methylphenyl maleimide / isobutene, and N-ethyl malei mide / N-(2, 6-diethyl phenyl) maleimide / isobutene, is desirable. As a combination of the maleimide system monomer comrade of a phenyl permutation, N-phenyl maleimide / N-methylphenyl maleimide / isobutene, N-phenyl maleimide / N-(2, 6-diethyl phenyl) maleimide / isobutene, etc. are desirable.

[0029] In addition, to the resin obtained in this invention, a hindered phenol, an anti-oxidant like organophosphate, a benzotriazol system ultraviolet ray absorbent, hindered amine system UV stabilizer, various lubricant, a color, etc. may be added if needed.

[0030] Furthermore to the resin of this invention, other resin and refractive-index differences in which this and compatibility are possible can also mix less than 0.02 thermoplastics, thermoplastic elastomer, a solid, or liquid rubber if needed.

[0031] Furthermore, in order to raise a mechanical characteristic, maintaining the optical property, resin and the inorganic bulking agent which has an equal refractive index substantially can also be mixed and used for the resin of this invention if needed.

[0032] Although such a bulking agent can be suitably chosen from the refractive index, the glass fiber (common-name E glass fiber) which consists of aluminosilicate glass which uses the oxide of silicon and aluminum as a principal component, for example, powder, a paste, microphone ****-**, a micro rod, a micro disk, etc. are mentioned.

[0033] As an approach of fabricating the resin of this invention, the usual shaping approaches, such as an injection-molding method, an extrusion method, compression forming, a blow molding method, and the spin cast method, are mentioned.

[0034] The obtained mold goods can be used to fields, such as an optical lens, an optical fiber, an optical disk and a substrate of an optical card, prism, lenses for automobiles, lenses for signals, and lighting components.

[0035] As an optical lens, the spherical surfaces, such as a compact disk lens, a lens for videos, and a lens for cameras, aspheric lenses, a glass lens, etc. are mentioned. The optical material of this invention The light transmission demanded as these lenses For example, 80% or more, It is 90% or more preferably, and a refractive index is 1.50 or more preferably 1.49 or more. The Abbe number is 45 or more preferably 35 or more. Glass transition temperature 100 degrees C or more, Preferably, especially, it is 140 degrees C or more preferably, and coefficient of linear expansion is -one or less 6x10 to 5 degree C especially preferably preferably -one or less 7x10 to 5 degree C -one or less 10x10 to 5 degree C, and surface hardness may also satisfy 120 degrees C or more also of properties more than H.

[0036]

[Example] Although an example explains this invention below, this invention is not limited to an example.

[0037] The weight average molecular weight of the generated copolymer was calculated by polystyrene conversion using GPC (HLC[by TOSOH CORP.]-802A).

[0038] Tg of the generated copolymer was measured with the programming rate of 10 degrees C / min. among nitrogen using DSC200 made from SEIKO Electron.

[0039] Light transmission is ASTM. Based on 1746, the refractive index was measured using the ABBE refractive-index meter.

[0040] The birefringence of the generated copolymer examined the photoelastic coefficient of a melting condition, i.e., an apparent birefringence, using the value which **(ed) with stress. The OPUTO rheometer by ORC Manufacturing Co., Ltd. and model HRS-100 were used for measurement of a photoelastic coefficient. After heat-treating the 40x10x0.4mm heat press test piece in the vacuum at Tg+20 degree C for 24 hours and removing orientation, in Tg+30 degree C, the photoelastic coefficient at the time of uniaxial stretching was measured.

[0041] After teaching N-(2, 6-diethyl phenyl) maleimide 129.4g and 2, 2'-azobisisobutyronitril (azobisuisobutironitoriru) 0.51g, and toluene 400ml to 1l. autoclave to which example 1 agitator, nitrogen installation tubing, isobutene installation tubing, a thermometer, and degassing tubing were attached and purging several times with nitrogen, liquefaction isobutene 228ml was taught and the

polymerization was performed at 60 degrees C for 8 hours.
[0042] The superfluous methanol was filled with reaction contents, the copolymer was deposited, and the copolymer was separated by filtering. It dried at 60 degrees C under reduced pressure after reprecipitation purification by toluene / methanol system for 24 hours. Yield was 160g.
[0043] The weight average molecular weight of the obtained copolymer was 280000, and the maleimide unit in a copolymer was 50-mol % from the result of elemental analysis.
[0044] After teaching N-(2-methylphenyl) maleimide 130.6g, par butyl neodecanate 0.24g, and toluene 500ml to the reactor given in example 2 example 1 and purging several times with nitrogen, liquefaction isobutene 284.5ml was taught and the polymerization was performed at 60 degrees C for 5 hours.
[0045] The yield of the obtained copolymer was 160g. The weight average molecular weight of the obtained copolymer was 240000, and the maleimide unit in the copolymer generated from the result of the elemental analysis of the sample refined according to reprecipitation was 50-mol %.
[0046] After teaching N-(2, 6-diethyl phenyl) maleimide 80.9g, N-methyl maleimide 39.2g, par butyl neodecanate 0.24g, and toluene 500ml to the reactor given in example 3 example 1 and purging several times with nitrogen, liquefaction isobutene 284.5ml was taught and the polymerization was performed at 60 degrees C for 5 hours.
[0047] The yield of the obtained copolymer was 152g. The weight average molecular weight of the obtained copolymer was 270000, the ratio of N-(2, 6-diethyl phenyl) maleimide unit in the copolymer generated from the result of 1 H-NMR measurement of the sample refined according to reprecipitation and ultimate analysis and N-methyl maleimide unit was 1/1 (mole ratio), and the maleimide unit in a copolymer was 50-mol %.
[0048] After teaching N-(2-methylphenyl) maleimide 106g, N-methyl maleimide 16g, par butyl neodecanate 0.24g, and toluene 500ml to the reactor given in example 4 example 1 and purging several times with nitrogen, liquefaction isobutene 284.5ml was taught and the polymerization was performed at 60 degrees C for 5 hours.
[0049] The yield of the obtained copolymer was 155g. The weight average molecular weight of the obtained copolymer was 270000, the ratio of N-(2-methylphenyl) maleimide unit in the copolymer generated from the result of 1 H-NMR measurement of the sample refined according to reprecipitation and ultimate analysis and N-methyl maleimide maleimide unit was 4/1 (mole ratio), and the maleimide unit in a copolymer was 50-mol %.
[0050] After teaching N-phenyl maleimide 122.9g, par butyl neodecanate 0.24g, and toluene 500ml to the reactor given in example 5 example 1 and purging several times with nitrogen, liquefaction isobutene 284.5ml was taught and the polymerization was performed at 60 degrees C for 5 hours.
[0051] The yield of the obtained copolymer was 151g. The weight average molecular weight of the obtained copolymer was 3 million, and the maleimide unit in the copolymer generated from the result of the elemental analysis of the sample refined according to reprecipitation was 50-mol %.
[0052] As an example of example of comparison 1 comparison, PMMA (AKURI pet; Mitsubishi Rayon Co., Ltd. make) was used. The glass transition temperature of PMMA was 105 degrees C. In addition, the value of optical physical properties was shown in Table 1.
[0053] As an example of example of comparison 2 comparison, PC (pan light AD9000TG; Teijin formation Make) was used. The glass transition temperature of PC was 141 degrees C. In addition, the value of optical physical properties was shown in Table 1.
[0054]
[Table 1]

h g cg b eb cg e e

	光線透過率 (%)	光弾性係数C $\times 10^{12}$ (cm^2 /dyne)	屈折率	ガラス転移温度 (℃)
実施例1	92	−160	1.550	204
実施例2	92	− 12	1.564	209
実施例3	92	+ 40	1.543	177
実施例4	92	+ 30	1.557	197
実施例5	89	+ 30	1.574	190
比較例1	92	− 6	1.491	105
比較例2	88	+700	1.585	141

[0055]
[Effect of the Invention] The copolymer of this invention is transparent, and has low form birefringence, and is further excellent in thermal resistance, surface hardness, and a mechanical strength as stated above. Therefore, the copolymer of this invention is useful as an optical material.

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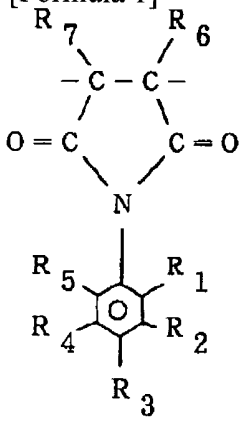
CLAIMS

[Claim(s)]
[Claim 1] At least one or more kinds of N-phenyl permutation maleimide units expressed with the following general formula (I), It is the copolymer which consists of an alpha olefin unit expressed with at least one or more kinds of N-alkyl maleimide units and the general formulas (III) which are expressed with the following general formula (II). The maleimide system copolymer whose 30 - 98-mol % and (III) the mole ratios of (I)/(II) are [a copolymerization presentation] 100 / 0 - 1/99 at 70 - two-mol % for ((I)+(II)) and whose weight average molecular weight of polystyrene conversion is 5x106 or less [1x103 or more].
[Formula 1]



(I)

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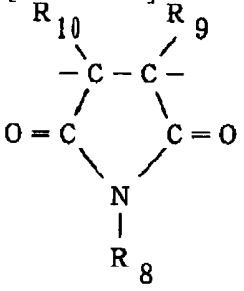

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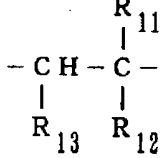
[Formula 3]



(III)

h g cg b eb cg e e h g

(R1, R2, R3, R4, R5, R6, R7, R8, R9, and R10 are the shape of a straight chain and the letter alkyl groups of branching of hydrogen, a halogen system element, a carboxylic acid, or carbon numbers 1-8 respectively, and R11, R12, and R13 show hydrogen or the alkyl group of carbon numbers 1-6 respectively here)
[Claim 2] The optical material characterized by consisting of a copolymer according to claim 1.

[Translation done.]

h g cg b eb cg e e h g